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From Electronic Structure to Catalytic Activity: A Single Descriptor for Adsorption and Reactivity on Transition-Metal Carbides

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Adsorption and catalytic properties of the polar (111) surface of transition-metal carbides (TMC's) are investigated by density-functional theory. Atomic and molecular adsorption are rationalized with the concerted-coupling model, in which two types of TMC surface resonances (SR's) play key roles. The transition-metal derived SR is found to be a single measurable descriptor for the adsorption processes, implying that the Brønsted-Evans-Polanyi relation and scaling relations apply. This gives a picture with implications for ligand and vacancy effects and which has a potential for a broad screening procedure for heterogeneous catalysts.

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New simple, efficient, and cheap catalysts might help to solve urgent environmental challenges [1], e.g., to harvest solar energy [2]. A goal in catalysis research is to design and tune the activity and selectivity of catalysts by controlling their structural properties at the atomic level. This calls for an identification of key concepts from fundamental theory, e.g., density-functional theory (DFT), as shown for transition-metal (TM) surfaces [3].

For such surfaces, the important role of the TM *d* electrons for chemisorption and catalysis was early anticipated [4], estimated [5], and articulated in the *d*-band model [3,6], establishing relations between atomic structure and activity for TM catalysts [7]. The *d*-band model explains and predicts a variety of TM properties, e.g., adsorption energies on TM alloys, bond strengths at steps and terraces, and transition-state energies [3,7], by correlating them to the energy of the *d*-band center. Its success has led to the introduction of simple descriptors that rationalize the experimental data [3]. Examples of such descriptors, e.g., for the water gas shift reaction, are the adsorption energies of oxygen and carbon monoxide on TM surfaces. Today, design of new TM catalysts by computational screening is a realistic approach [8,9].

A need for catalysts, a scarcity of precious catalyst materials, and a general curiosity spur the interest in catalyst materials beyond the TM's. Statements like "for several types of reactions, such as hydrogenation reactions, catalytic activities of carbides and nitrides were approaching or surpassing those of noble metals" can be found in the literature [10]. Thus, a theoretical approach extended to more complex materials than TM's is of interest. In a study of H adsorption on TM-terminated (111) surfaces of TM carbides (TMC's), a deviation from the *d*-band model has been observed [11]. A recent study of TM oxides, nitrides, and sulfides stresses similarities in scaling behavior between molecular and atomic adsorption energies but calls for "a suitably modified *d*-band model" [12]. There exist suggestions of a bulk-derived descriptor for the reactivity of the TMC's [13]; however, our work goes beyond and finds a surface-derived descriptor based on electronic-structure calculations.

Electronic surface states and resonances (SR's), known to appear at steps and defects, play an important role for the catalytic activity of a system. The ideal and stable TMC(100) faces are common objects of study in the literature [14] and do not show any presence of SR's. Recently we have shown that the understanding of atomic adsorption on TiC and TiN calls for substantial steps beyond the original *d*-band model [15–17]. On TiC(111) and TiN(111), the key actors are identified to be two types of SR's, derived from Ti (TiSR) and C(N) states (CSR/NSR), respectively. The adsorption mechanism is explained within a concerted-coupling model (CCM), in which two types of interactions are involved, one between the adsorbate and the TiSR and one between the adsorbate and the CSR's (NSR's) [15–17]. The presence of SR's motivates a focus on the metastable and polar TMC(111) surfaces, which may, for example, serve as prototypes for steps and defects.

This Letter demonstrates how DFT calculations, trend studies, analyses of computed results in electron-structural terms, formulation of a model, and utilization of model predictions [15–17] can be used to reach the goal above. In terms of the CCM, we identify a single descriptor, the mean energy of the TM-localized SR (TMSR), that accounts for three important processes on the considered TMC surfaces: adsorption, dissociation, and catalytic activity. The results should be general but are here illustrated for one surface reaction, the ammonia synthesis. As a consequence of the single descriptor, calculable and experimentally available for some substrates [18], scaling relations and Brønsted-Evans-Polanyi (BEP) relations are

shown to apply, in the same way as for TM surfaces [3]. The generality and practical usefulness of the conceptual picture is demonstrated by applications to pure TM surfaces, and to ligand and defect effects, which also indicate possibilities for further refinements. Taken together, these results provide a framework for a systematic analysis of the catalytic activity of the TMC's.

Trend studies are conducted for the catalysis-relevant adsorbates H, N, O, and NH_x ($x = 1, 2, 3$), with respect to the TM component of the substrate TMC, spanning three different periods and four different groups in the periodic table (TM = Sc, Ti, V, Zr, Nb, Mo, Ta, and W) [19]. The first-principles study is performed within DFT, as implemented in DACAPO [20,21]. The computational procedures are favorably tested and compared with literature data [22]. From the DFT calculations, the adsorption is described in terms of adsorption energies (E_{ads}) and atom-projected local densities of states (LDOS).

Calculated total density of states (DOS) and LDOS's for the TM-terminated TMC(111) surfaces (illustrated for some representative cases in Fig. 1) reveal the existence of SR's on all these surfaces. There is a TMSR in the vicinity of the Fermi energy (E_F) and several carbon-localized SR's (CSR's) deeper down in the valence band [23]. Note that ScC(111) has no filled TMSR states.

The TMSR's are characterized by studying the difference in bulk and surface DOS's [23], where they appear as positive peaks owing to the build up of states at the surface. A parameter ε_{CCM} is defined as the mean energy (center of gravity) of the TMSR, in close analogy with the d-band center ε_d in the d-band model. The integration is performed over the energy range of the positive TMSR peak. The value of ε_{CCM} decreases as the group number of the TM component increases (Fig. 1), as expected from the filling of the TM d states [23].

Analysis of the DOS before and after adsorption (illustrated for O/VC in the lower panel of Fig. 1) shows that the TMSR is depleted upon adsorption. This supports the CCM assumption that only the surface-localized part of the d-band spectrum is relevant for the adsorption and that the TMSR's are key actors in the adsorbate-surface interaction [23]. Hence, ε_{CCM} is a descriptor for the atomic adsorption on TMC's. An exception is ScC, with its empty TMSR and consequently an adsorption mainly arising from the interaction with the CSR's [23]. This exception confirms the presence of two types of interactions, as formulated in the CCM [15–17,23].

The role of ε_{CCM} as a descriptor is confirmed by extensive DFT calculations, which yield a linear correlation between the E_{ads} and ε_{CCM} values for each of the studied adsorbates (Fig. 2). The E_{ads} value decreases (i.e., the adsorption gets stronger) as ε_{CCM} increases, with a gradient that varies strongly between different adsorbates. The slopes of the E_{ads} vs ε_{CCM} correlations are steeper for the TMC(111) surfaces than for TM's [3]. From a design perspective, this could be a useful property, allowing larger effects from small changes. Again, ScC does not follow the

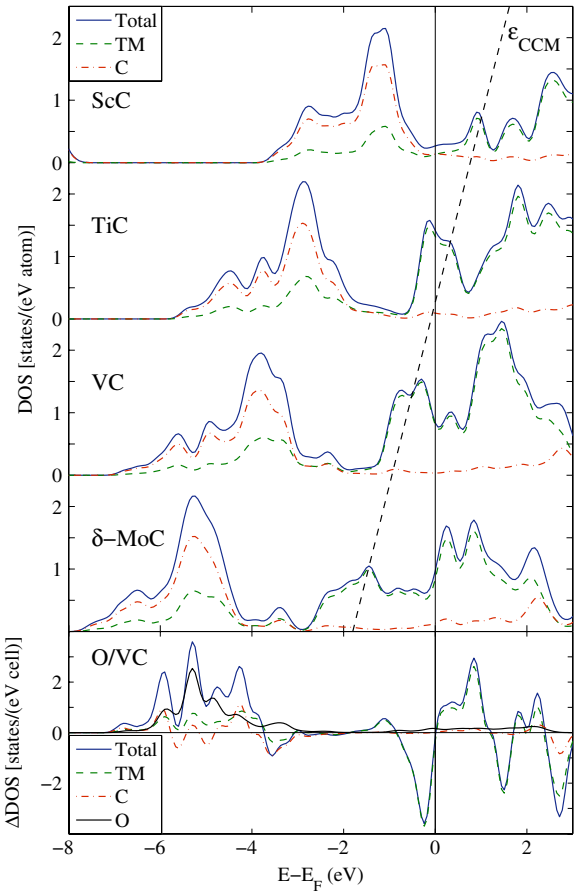

FIG. 1 (color online). Upper panel: Calculated atom-projected and total (111) surface DOS's for a group of TMC's. The dashed diagonal line connects the mean energies ε_{CCM} of the TMSR's and illustrates the downward shift of the TMSR energy along the TMC series as the group number of the TM component increases. Lower panel: Difference in surface DOS induced by O adsorption on VC(111).

trend of the other TMC's, reflecting the different nature of its interaction with the adsorbate.

To further test that proper key concepts (TMSR and ε_{CCM}) have been identified, ligand effects are studied. Manipulating the local environment of the surface TM atom changes ε_{CCM}, thereby changing adsorption, activation, and other energies, which opens up for optimization of the catalytically active site. In our illustrative example, O adsorption on a TiC(111) surface with one, two, or three surface Ti atoms next to the fcc adsorption site replaced by V atoms, the calculated adsorption strength is successively reduced at the same time as the local value of ε_{CCM} is shifted down. This is expected in the CCM (exchange of Ti with V shifts d levels down in energy) and monitored by analyzing our calculated LDOS's.

However, there is a deviation from the linear E_{ads} vs ε_{CCM} relation [24]. For example, the E_{ads} value for the system with three neighboring V atoms on the TiC(111) surface is similar to that for pure VC(111), although their ε_{CCM} values differ. This ligand calculation points at further

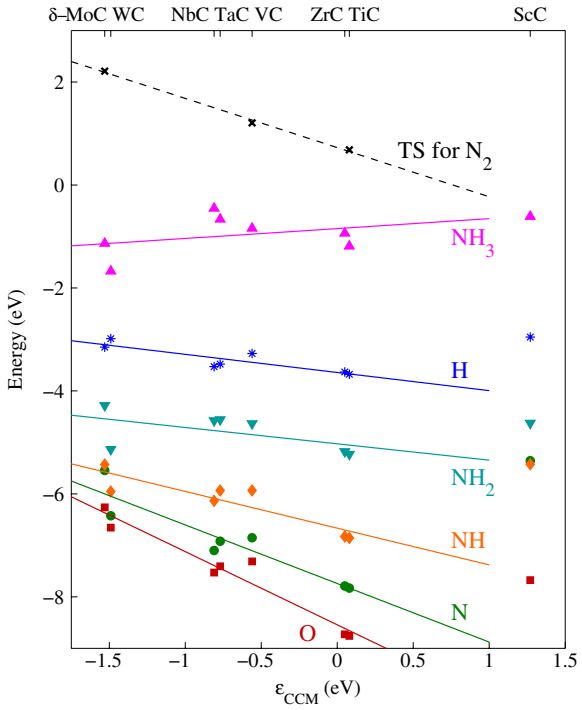

FIG. 2 (color online). Adsorption energies of H, N, O, and NH_x ($x = 1, 2, 3$) on the considered TMC(111) surfaces vs the descriptor ε_{CCM} (the TMSR center of mass). The adsorption energy is defined as $E^A_{ads} = E_{TMC+A} - E_{TMC} - E_A$ for each adsorbate A. (ScC is not included in the linear regressions.) Also included (dashed line) are the transition-state (TS) energies for N_2 dissociation, calculated with a fixed bond-length method.

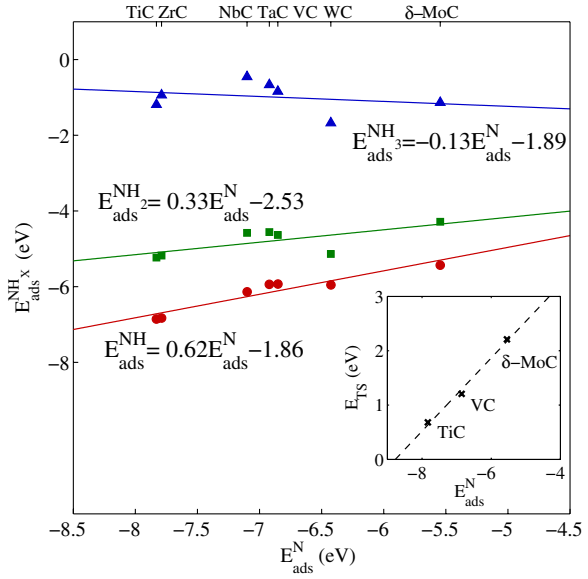

FIG. 3 (color online). Adsorption energies on TMC(111) surfaces (ScC is not included) for NH_x ($x = 1, 2, 3$) vs N atomic adsorption energies (scaling relation). The adsorption energy is defined as $E^{NH_x}_{ads} = E_{TMC+NH_x} - E_{TMC} - E_{NH_x}$. Inset: the linear variation of the activation energy for N_2 dissociation (E_{TS}) vs N atomic adsorption energy on TiC, VC, and δ-MoC (BEP relation).

possible refinements of the descriptor. An orbital projected DOS shows that the main interaction takes place between the adsorbate and the d_{xz+yz} components of the TMSR (the z direction being perpendicular to the surface). Hence a refined descriptor, taken as the center of mass of these levels, could be introduced. However, such a detailed descriptor level might not be practical from an experimental point of view.

As ε_{CCM} is a descriptor for both atomic and molecular adsorption (Fig. 2), there is a scaling relation between the molecular and atomic E_{ads} values (Fig. 3). Similar scaling relations have been found for several molecular species on TM's [25], and for OH_x on TM oxides, NH_x on TM nitrides, and SH_x on TM sulfides [12]. These can be described by a linear equation $E^{AH_x}_{ads} = \gamma(x)E^A_{ads} + \xi$, where $\gamma(x)$ depends on the number x of H atoms in the molecule [3]. Our results (Fig. 3) yield values ($\gamma_{NH} = 0.62$, $\gamma_{NH_2} = 0.33$, $\gamma_{NH_3} = -0.13$) that are close to the predictions 2/3, 1/3, and 0 for $x = 1$, 2, and 3, respectively. The small deviations are likely caused by the C species in the substrate, which influences the adsorption mechanism directly via the CSR's and indirectly via the interaction with the TM species [11,15–17].

In heterogeneous catalysis, linear correlations (BEP relations) between activation and adsorption energies play an important role [3]. Activation energies for N_2 dissociation on some TMC(111) surfaces [26], calculated as the transition-state energy barriers (E_{TS}) by use of a fixed bond-length method, are presented in the inset of Fig. 3 as a function of the N adsorption energy. They show that the BEP relation holds for the TMC's, as expected from the linear correlation between the activation energies and ε_{CCM} (dashed line in Fig. 2). The result is expected to apply generally, as variations in activation and adsorption energies are governed by the same basic mechanism, which for TM's is the d-band model [3] and for TMC's the CCM [15–17,23].

The linear dependence of both adsorption and activation energies on ε_{CCM} opens up the possibility to design the TMC substrates using the CCM to suit different catalytic reactions. This can be illustrated by the ammonia synthesis ($N_2 + 3H_2 \rightleftharpoons 2NH_3$), which is a commonly used reaction to develop new concepts and ideas in catalysis [27]. By using a slightly modified microkinetic model [28,29] the calculated catalytic activities of the TMC's are found to order as a volcano curve with respect to the single descriptor ε_{CCM} [30].

The general importance of TMSR's for surface reactions and the generality of our approach is strengthened by applying it to a selected group of pure TM(111) surfaces [31]. In the same way as for the TMC's, the descriptor ε_{CCM} is determined by studying the difference in surface and bulk DOS's, identifying the positive regions, and calculating the mean energy of this positive region. Only a certain part of the d band (the surface-localized states in

the upper part of the valence band) is found to be important for understanding the trends between different TM's. The trend in reactivity can be rationalized by using $\varepsilon_{\mathrm{CCM}}$ just as well as ε_d of the original d-band model [31]. This finding stimulates further investigations on this group of materials.

SR's can also appear on stable surfaces near defects, such as vacancies, steps, and adsorbed clusters. For example, experimental studies show that oxygen atoms replace carbon atoms on TiC(100) and ZrC(100) surfaces when exposed to O_2 [14,32]. Our calculations on an O atom adsorbed in a C vacancy site on the TiC(100) surface show the presence of a pronounced TMSR localized around the C vacancy. The calculated adsorption energy (-8.71 eV) is close to the value on the TiC(111) surface (-8.76 eV), to be compared with the value (-4.96 eV) on the vacancy-free TiC(100) surface, where no TMSR is present. Based on our findings, the descriptor $\varepsilon_{\mathrm{CCM}}$ is expected to be directly applicable for understanding processes on other TM compound surfaces (and probably even on other surfaces) with SR's similar to the ones on the TMC(111) surface.

Taken together, our results provide a framework for a systematic analysis of the catalytic activity of the TMC's. We have shown that by theoretical means it is possible to find a single descriptor, corroborated by experimental results on the electronic structure of the TMC surfaces [18], for atomic and molecular adsorption, as well as for a simple reaction on the TMC's. The found scaling and BEP relations provide simple and efficient connections between the (local) surface electronic structure and its reactivity, of importance for studying defect (e.g., vacancy) and ligand effects. There are thus implications for surfaces, nanosystems, and catalysis, and the introduced concepts should ramify to other systems and stimulate the development of similar models for other classes of materials.

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